PATENT SPECIFICATION

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COMPLETE SPECIFICATION

A process of Curing Siloxane Resins

We, MIDLAND SILICONES LIMITED, a British Company, of 19 Upper Brook Street, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process of curing completely condensed organosiloxane resins.

It has long been known that organosiloxane resins make excellent high temperature coatings for metal and other surfaces. It has also been known that these coatings tend to be more corrosion resistant than do similar coatings made from organic materials. However, the organosiloxane coatings heretofore employed, especially those which contain only organosilicon resins, require higher temperatures and longer curing time than is needed for most organic finishes. In general, organosilicon resins heretofore commercially available protect metal and glass surfaces from corrosion better in most cases than organic resins. However, these previously employed organosilicon resins leave much to be desired in the way of protection for metal surfaces under rigid conditions such as those encountered in sea water and the like.

It is known that completely condensed organosiloxanes, i.e., siloxanes containing no silicon bonded hydroxyl groups, could be employed for coating base members. However, as is shown in Specification No. 688,192, these materials require even higher temperatures and more prolonged curing schedules than the more commonly employed hydroxylated siloxane resins. The present invention provides a process of curing siloxane resins which obviates the above difficulties.

It is an object of this invention to provide a process of curing completely condensed organosiloxane resins at sufficiently low temperatures and in a sufficiently short period of time so that the curing will be commercially feasible. Another object is to provide superior silicone resin coatings for metal and other surfaces.

[*Price 3s. 6d.*]

This invention provides a method of curing completely condensed co-polymeric siloxanes containing from 5 to 75 mol % siloxane units of the general formula $XR_nSiO_{\frac{3-n}{2}}$ wherein X is the functional radical HOR^1— or the functional radical $(YOOC)_aR^{11}$— in which R^1 is a divalent saturated aliphatic or cycloaliphatic hydrocarbon radical containing at least 3 carbon atoms, the hydroxyl group being attached to a carbon atom which is at least three carbon atoms away from the silicon, R^{11} is a divalent or trivalent saturated aliphatic or cycloaliphatic hydrocarbon radical containing at least three carbon atoms wherein each carbonyl group is attached to a carbon atom which is at least three carbon atoms away from the silicon atom, Y is an alkyl radical or a hydrogen atom and *a* is 1 or 2, R is a monovalent hydrocarbon radical free from aliphatic unsaturation or a halogenated monovalent hydrocarbon radical free from aliphatic unsaturation or a mixture thereof, and *n* has an average value from 0 to 2, the remainder of the siloxane being composed of siloxane units of the general formula $Z_mSiO_{\frac{4-m}{2}}$ in which Z is a monovalent hydrocarbon radical or a halogenated monovalent hydrocarbon radical or a mixture thereof and *m* has an average value from 0 to 3 inclusive and in which co-polymeric siloxane the average ratio of total organic groups to silicon ranges from 1 to 1.7, by heating a mixture of said siloxane and a poly-functional organic curing compound capable of condensing with the X groups in the siloxane to give cross linking, until the siloxane is cured.

In carrying out the process of this invention it is only necessary to mix the siloxane and the polyfunctional organic curing compound in the desired proportions and thereafter heat until a satisfactory cure is obtained. The curing temperatures vary with the reactants employed but can range from 30° C. up to 250° C. or higher. In general, satisfactory cures can be obtained in the temperature range

from 100—150° C. for periods of 30 minutes or less. The curing operation can be either a one step or a multiple step process. Thus the mixture of siloxane and organic curing compound can be partially reacted and the product thereafter moulded or applied as a coating and the curing completed by further heating. Alternatively, the mixture can be heated continuously until a satisfactory cure is obtained.

The process of this invention is particularly adaptable for the application of siloxane protective coatings in which the base member is dipped in a mixture of the siloxane and the curing compound and thereafter heated until the film is cured.

The proportions of the functional units $XR_nSiO_{\frac{3-n}{2}}$ in the siloxane should be at least 5 mol % in order to obtain satisfactory cures. The upper limit will be determined by the thermal stability desired in the finished product. If a high degree of thermal stability is desired, the organofunctional siloxane units should be present in amount of 5 to 20%. This reduces the amount of organic material present in the resin and hence the stability of the cured film is essentially the same as that of conventional silicone resins. If thermal stability is not the primary factor in the final product, higher amounts of the organofunctional siloxanes with a proportional increase in the amount of organic curing agent can be employed.

It should be understood that siloxanes containing both silicon bonded OH groups and the X groups above defined can be cured by heating them with organofunctional curing agents.

Our Specification No. 769,497 claims organopolysiloxanes containing polymeric units of the general formula $(HOR)R^1_bSiO_{\frac{3-b}{2}}$ where R is a divalent saturated aliphatic or cycloaliphatic hydrocarbon radical containing at least three carbon atoms, the hydroxyl group being attached to a carbon atom which is at least three carbon atoms from the silicon, R^1 is a monovalent hydrocarbon or halogenated monovalent hydrocarbon radical free from aliphatic unsaturation and b is 0 or 1. The said Specification also claims co-polymeric organosiloxanes composed of units of the aforesaid general formula $(HOR)R^1_bSiO_{\frac{3-b}{2}}$ and units of the general formula $R^{11}_nSiO_{\frac{4-n}{2}}$ where each R^{11} is a monovalent hydrocarbon radical or a halogenated monovalent hydrocarbon radical and n is 1 to 3 inclusive. The said Specification further claims a process for the manufacture of organosilicon-modified organic resins which comprises reacting (1) an organopolysiloxane containing polymeric units of the aforesaid general formula $(HOR)R^1_bSiO_{\frac{3-b}{2}}$ with (2) one or more polyfunctional organic compounds normally employed in resin production such as di-isocyanates, di-carboxylic acids or di-carboxylic acid anhydrides or one or more functional siloxanes as described in Specifications Nos. 769,496 and 769,498.

Our Specification No. 769,496 claims an organopolysiloxane containing polymeric units of the general formula $[(YOOC)_aR]R^1_bSiO_{\frac{3-b}{2}}$ wherein Y is an alkali radical or a hydrogen atom, a is 1 or 2, R is a divalent or trivalent saturated alicyclic hydrocarbon radical or a saturated alicyclic divalent or trivalent hydrocarbon radical, in which each carbonyl group is attached to a carbon atom which is at least three carbon atoms away from the silicon, R^1 is a monovalent hydrocarbon radical or a halogenated monovalent hydrocarbon radical, said R^1 radicals being free from aliphatic unsaturation and b is 0 or 1. The said Specification No. 769,496 also claims a co-polymeric siloxane compound of units of the aforesaid general formula $[(YOOC)_aR]R^1_bSiO_{\frac{3-b}{2}}$ and units of the general formula $R^{111}_mSiO_{\frac{4-m}{2}}$ where each R^{111} is a monovalent hydrocarbon radical or a halogenated monovalent hydrocarbon radical and m is 1 to 3 inclusive. The said Specification No. 769,496 further claims a process for the manufacture of organosilicon-modified organic resins comprising reacting (1) an organopolysiloxane containing polymeric units of the aforesaid general formula

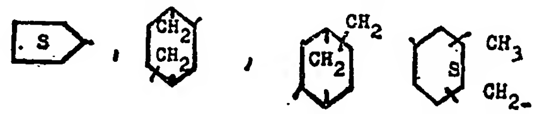
$$[(YOOC)_aR]R^1_bSiO_{\frac{3-b}{2}}$$

with (2) one or more polyfunctional organic compounds containing organicfunctional groups capable of reacting with the (YOOC—) radical of the aforesaid organopolysiloxane e.g. a compound in which the functional group is an acid group, ester group, hydroxyl radical or amine radical, or a polyhydric alcohol or a polyamine or (3) with another organopolysiloxane containing such organic functional groups.

The process of the said Specifications Nos. 769,496 and 769,497 do not result in completely condensed siloxanes, thus for example the process of Example 10 of Specification No. 769,496 which uses a dilute aqueous alcoholic alkali solution does not result in the production of a completely condensed siloxane.

If desired the siloxanes employed herein can contain one or more than one type of $XR_nSiO_{\frac{3-n}{2}}$ units. In those organofunctional siloxanes in which X is a hydroxylated radical, R^1 can be any saturated aliphatic divalent hydrocarbon radical containing at least 3 car-

bon atoms such as propylene, butylene and octadecylene and any saturated cycloaliphatic divalent hydrocarbon radical containing at least 4 carbon atoms such as



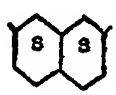
In the organofunctional siloxanes in which X is a carboxylated radical, R^{11} can be any divalent saturated aliphatic hydrocarbon radical containing at least 3 carbon atoms such as propylene, butylene and octadecylene or any trivalent aliphatic saturated hydrocarbon radical containing at least 3 carbon atoms such as

$$—CH_2CH_2\overset{|}{C}HCH_2CH_2—,$$

$$—(CH_2)_5\overset{|}{C}H(CH_2)_5—$$

$$\text{and } —(CH_2)_2\overset{|}{C}H(CH_2)_6—$$

or any cyclic divalent aliphatic hydrocarbon radical containing at least 5 carbon atoms such as cyclohexylene, cyclopentylene, methylcyclopentylene, and



and any trivalent cycloaliphatic saturated hydrocarbon radical containing at least 6 carbon atoms such as

It should be understood that the term carboxyl group as employed herein includes the group COOH and COOY in which Y is an alkyl radical such as methyl, ethyl or octadecyl.

In the organofunctional siloxane units R can be any monovalent hydrocarbon radical free from aliphatic unsaturation such as alkyl radicals such as methyl, ethyl and octadecyl; cycloalkyl radicals such as cyclohexyl and cyclopentyl and aromatic hydrocarbon radicals such as phenyl, benzyl, tolyl, naphthyl and xenyl. R^1 can also be any halogenated monovalent hydrocarbon free from aliphatic unsaturation such as chlorophenyl, dibromoxenyl, tetrafluoroethyl, pentafluorobutyl and α,α,α-trifluorotolyl.

For the purpose of this invention the organosiloxanes of the general formula

$$Z_nSiO_{\frac{4-n}{2}}$$

can be any siloxane in which Z is any monovalent hydrocarbon radical such as alkyl radicals such as methyl, ethyl and octadecyl; alkenyl radicals such as vinyl and allyl; cycloaliphatic radicals such as cyclohexyl, cyclopentyl and cyclohexenyl and aromatic hydrocarbon radicals such as phenyl, benzyl, tolyl, naphthyl and xenyl and any halogenated monovalent hydrocarbon radical such as chlorophenyl, trifluorovinyl, tetrafluorobutyl, tetrabromoxenyl and α,α,α-trifluorotolyl. The siloxanes can be either homo-polymers or copolymers and there can be more than one type of Z group attached to any one silicon atom and the units can be $ZSiO_{1.5}$, Z_2SiO and $Z_3SiO_{0.5}$ together with limited amounts of SiO_2 units.

The relative proportions of the siloxanes and the polyfunctional organic curing compounds are not critical. Obviously, however, the most efficient operation will be obtained when the organic curing agent is employed in amounts approximately equivalent to the functional X groups in the siloxane. Thus the most efficient operation will usually occur in the range from that in which the organic curing compound is present in amount such that there is one of its functional groups for every OH, COOH and COOY group in the siloxane to that in which there is one mol of organic curing compound per mol of $XR_nSiO_{\frac{3-n}{2}}$ units (i.e., as in Example 2).

The polyfunctional organic curing compounds which are employed in the process of this invention will vary depending upon the type of X group in the siloxane. In those cases where X is a hydroxylated radical, any hydroxyl reactive polyfunctional organic compound can be employed such as dicarboxylic acids such as maleic, phthalic, terephthalic, malonic and sabacic acids and their esters or anhydrides and diisocyanates such as *m*-toluene diisocyanate, *p,p*^{1} - diisocyanato - diphenylmethane and *p*-diisocyanato-benzene. The isocyanates are the preferred curing materials for the hydroxylated siloxanes. In those cases where X is an acid or ester group any polyfunctional organic compound which is reactive towards carboxylic acids or their esters can be employed. Specific examples of such compounds are polyhydric alcohols such as ethylene glycol, glycerine, pentaerythritol and polyamines such as ethylene diamine, octamethylene triamine, hexamethylene diamine and octadecylene diamine. The diamines are

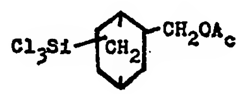
the preferred curing materials for the carboxylated siloxanes.

The superior qualities of the coatings formed by the process of this invention are specifically exemplified in their superior resistance to attack by chemical reagents. This is shown by the fact that metal surfaces which are coated with the resins prepared by the process of this invention show much less corrosion when exposed to salt water, caustic alkalies and acid than resins prepared from conventional organosiloxanes. The process of this invention is equally applicable for the preparation of siloxane moulding compositions, laminates and cast articles.

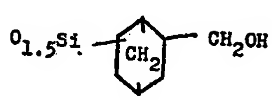
The following examples illustrate the invention.

EXAMPLE 1.

A mixture of 105 g. of phenylmethyldichlorosilane, 31.6 g. of phenyltrichlorosilane, 22.3 g. of methyltrichlorosilane and 45.2 g. of a mixture of isomers of the formula



were co-hydrolysed in the presence of toluene and ether. The resulting resin was then refluxed in a mixture of 100 ml. of toluene, 50 ml. of ethanol and 10 g. of potassium hydroxide for 3 hours at 81° C. The resulting product was a siloxane co-polymer resin composed of 55 mol % of phenylmethylsiloxane, 15 mol % of monophenylsiloxane, 15 mol % of monomethylsiloxane and 15 mol % of a mixture of isomers of the formula



A 70% toluene solution of this resin was mixed with an equivalent amount of *m*-toluene diisocyanate. Sheet iron panels were coated with this solution and cured for 30 minutes at 120° C. The films obtained were light in colour, glossy and flexible and were unaffected by hydrogen chloride and by saturated sodium chloride solution when heated in the latter 3 hours at 95° C.

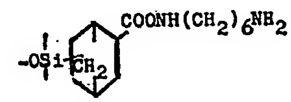
Equivalent results were obtained when the resin was reacted with p,p^1-diisocyanatodiphenylmethane.

EXAMPLE 2.

97 G. of phenylmethyldichlorsilane, 20.8 g. of methyltrichlorosilane and 29.4 g. of phenyltrichlorosilane, 19 g. of diphenyldichlorosilane and 40 g. of a mixture of isomers of the formula

were dissolved in 250 ml. of toluene and 154 ml. of diethyl ether and hydrolysed with water. During hydrolysis the mixture was cooled in an ice bath and made almost neutral with sodium hydroxide. The organic layer was washed until neutral, stripped of ether and azeotropically dried. It was then completely condensed by refluxing in 25% toluene solution for 6 hours with potassium hydroxide in an amount of 0.2% by weight calculated on the weight of the resin solids. The resulting solution was free from silicon-bonded hydroxyl groups and was neutralised, washed and dried. The solution was concentrated to 70% by weight of solids. The resulting siloxane was the co-polymer having the composition 50.8 mol % of phenylmethylsiloxane, 13.9 mol % of monomethylsiloxane, 13.9 mol % of monophenylsiloxane, 7.5 mol % of diphenylsiloxane and 13.9 mol % of a mixture of isomers of the formula

9.3 G. of the above co-polymeric siloxane (equivalent to 0.01 g.-mol) was mixed with 1.2 g. (0.01 g.-mol) of hexamethylene diamine and heated at 250° C. for 2 hours in a nitrogen atmosphere. The resulting viscous resin was dissolved in 5 g. of toluene. In this resin the carboxymethyl group had been converted into a mixture of isomeric amides having the formula



Panels of sheet iron were dip coated with a toluene solution of this resin (A) and were compared with a commercial phenylmethylpolysiloxane resin (B) having the composition 50.8 mol % of phenylmethylsiloxane, 27.8 mol % of monomethylsiloxane, 13.9 mol % of monophenylsiloxane and 7.5 mol % of diphenylsiloxane which contained about 1.5% of silicon bonded hydroxyl groups and a small amount of a zinc naphthenate catalyst. The panels were cured as shown in the table below and were immersed in a saturated aqueous sodium chloride solution at 90—95° C. and the effect on the film was noted as shown in the table. Plate glass was coated with resins (A) and (B) and the resulting panels cured as shown in the table below and then immersed in concentrated aqueous sodium hydroxide and toluene at 30° C. for the times shown.

TABLE I

Immersion Media	Resin	Curing Schedule	Results
Saturated aqueous NaCl	A	Air dried 15 min. 150° C. for 15 min. 250° C. for 15 min.	Unaffected in 4 hrs.
	B	Identical	Film blistered and broke in 4 hrs.
Concentrated aqueous NaOH	A	Air dried 15 min. 150° C. for 15 min. 250° C. for 1 hour	Unaffected in 3 days
	B	Identical	Film softened and loosened in 2 days
Toluene	A	Identical	Softened in 1 min.
	B	Identical	Completely dissolved in 1 min.

EXAMPLE 3.

Equivalent results were obtained when diethylene triamine was employed in the procedure of Example 2.

EXAMPLE 4.

When a completely condensed co-polymer having the composition of 5 mol .% of vinylphenylsiloxane, 50 mol % of dimethylsiloxane, 10 mol .% of chlorophenylsiloxane, 10 mol % of α,α,α-trifluorotolylsiloxane, 20 mol of monovinylsiloxane and 5 mol % of gamma-hydroxylpropylmethylsiloxane was reacted with *m*-toluene diisocyanate in accordance with the procedure of Example 1, satisfactory cure of the siloxane resin was obtained.

EXAMPLE 5.

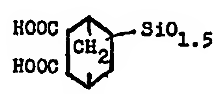
When a completely condensed co-polymer of 35 mol % of monophenylsiloxane and 65 mol % of the siloxane $ClC_6H_4\overset{O}{\overset{|}{Si}}(CH_2)_{10}COOH$ was heated with hexamethylene diamine in accordance with the procedure of Example 2 a cured siloxane resin was obtained.

EXAMPLE 6.

When a completely condensed co-polymeric siloxane of the composition 50 mol % of phenylmethylsiloxane, 35 mol % of monophenylsiloxane and 15 mol % of phenyl-gamma - hydroxypropylsiloxane was reacted with *m*-toluene diisocyanate in accordance with the procedure of Example 1, a cured siloxane was obtained.

EXAMPLE 7.

When a completely condensed co-polymer of 50 mol % of phenylmethylsiloxane, 25 mol % of α,α,α-trifluorotolylsiloxane and 25 mol % of a mixture of isomers of the formula



was mixed with hexamethylene diamine in an amount such that there was one amino group per one carboxyl group in the mixture and thereafter heated at 150° C. for 30 minutes, a cured siloxane resin was obtained.

WHAT WE CLAIM IS:—

1. A process of curing completely condensed organopolysiloxanes which comprises preparing a mixture of:

(1) A completely condensed co-polymeric siloxane containing:

(a) 5 to 75 mol per cent of siloxane units of the general formula $XR_nSiO_{\frac{3-n}{2}}$ wherein R is a monovalent hydrocarbon radical free from aliphatic unsaturation or a halogenated monovalent hydrocarbon radical free from aliphatic unsaturation, *n* has an average value of from 0 to 2 inclusive, X is the functional radical HOR^1— or the functional radical $(YOOC)_aR^{11}$—, in which R^1 is a divalent saturated aliphatic radical containing at least 3 carbon atoms or a divalent saturated cycloaliphatic hydrocarbon radical, with the hydroxyl group attached to a carbon atom which is at least three carbon atoms away from the silicon, R^{11} is a divalent or trivalent saturated aliphatic hydrocarbon radical containing at least 3 carbon atoms or a saturated cycloaliphatic hydrocarbon radical, with each carbonyl group attached to a carbon atom which is at least

three carbon atoms away from the silicon atom, Y is an alkyl radical or a hydrogen atom, and *a* is 1 or 2, and

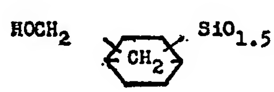
(b) 25 to 95 mol per cent of siloxane units of the general formula $Z_mSiO_{\frac{4-m}{2}}$ wherein Z is a monovalent hydrocarbon radical or a halogenated monovalent hydrocarbon radical and *m* has an average value of from 0 to 3 inclusive, said co-polymer of (a) and (b) having an average of from 1 to 1.7 inclusive total organic groups per silicon atom.

(2) A polyfunctional organic curing compound capable of condensing with the X groups in the siloxane to give cross linking,

and heating the mixture of (1) and (2) until the siloxane is cured.

2. A process as claimed in claim 1 wherein the completely condensed siloxane (1) contains 5 to 75 mol per cent of siloxane units of the general formula $(HOR^1)R_nSiO_{\frac{3-n}{2}}$ and R^1, R and *n* are as defined in claim 1, and the polyfunctional curing compound (2) is a diisocyanate.

3. A process as claimed in claim 2 wherein the completely condensed siloxane (1) is of the unit formula

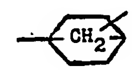


or $HOCH_2CH_2CH_2(CH_3)SiO$

and each Z in siloxane (2) is a phenyl radical or a methyl radical.

4. A process as claimed in claim 1 wherein the completely condensed siloxane (1) contains 5 to 75 mol per cent of siloxane units of the general formula $[(YOOC)_aR^{11}]R_nSiO_{\frac{3-n}{2}}$ and Y, R^{11} R, *n* and *a* are as defined in claim 1, and the polyfunctional curing compound (2) is a diamine.

5. A process as claimed in claim 4 wherein Y is a methyl radical, *a* is 1, R^{11} is the divalent radical



and *n* is 0, and Z is a methyl radical, a phenyl radical or both.

6. A process of curing completely condensed organopolysiloxanes substantially as described with reference to any one of the Examples.

7. Cured organopolysiloxanes when produced by the process claimed in any one of the preceding claims.

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